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POLLUTANT ADSORBENT SYSTEMS FOR TNT RDX AND HMX IN
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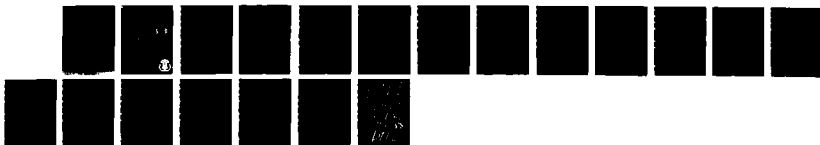
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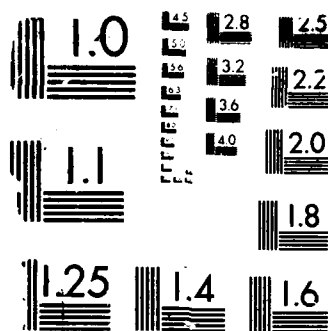
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TECHNICAL REPORT 8605

POLLUTANT ADSORBENT SYSTEMS FOR TNT, RDX, AND HMX IN WASTEWATER

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RAMCHANDRA K. KULKARNI, Ph.D.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → Silica gels were prepared in the presence and absence of the pollutants TNT, RDX, and HMX (separately), and purified by exhaustive elution with methanol and acetonitrile. Gels prepared in the presence of TNT or RDX consistently showed enhanced adsorptive power for the homologous pollutant. The same was not true with HMX because of its very limited solubility. These		

20. Abstract (continued)

gels, when their hydroxyl groups were capped with trimethylchlorosilane, exhibited the same higher adsorptive power. The relative adsorptive power (selective/control) was less than 2. Thus, the adsorption was still too small for practical use in detection or removal of these pollutants from wastewater. Cross-linked acrylic polymers were similarly prepared in the presence of TNT, RDX, and HMX. These new polymers did not show any trend of increased adsorption in the case of TNT and RDX, perhaps because of high chain-transfer and inhibitive properties of TNT and RDX in the free radical polymerization. However, HMX-modified cross-linked polyacrylates did show a reasonable increase in adsorptivity over the normal control cross-linked polymer.

PREFACE

This research on pollutant adsorbent systems was modeled on previous research by the author on silica gel and polyacrylate adsorbents specific for pesticides. In this, as in the earlier work, adsorption by silica gels and polyacrylates was estimated from the solution concentrations of adsorbate, determined before and after adsorption.¹⁰



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INTRODUCTION

Small quantities of the explosives TNT, RDX, and HMX and such co-products as TAX, SEX, and dinitrotoluenes are released in effluent waters from the large-scale manufacture of high explosives by Army ammunition plants. The proposed limits, or ambient discharge criteria, are 0.06 mg/L of TNT, 0.3 mg/L of RDX, and 0.3 mg/L of HMX.¹ See Table 1 for names of chemicals referred to or used in the investigation.

Although primary and biological secondary treatments are given to wastewater by the industrial liquid waste treatment facilities, the pollutants still escape, making it necessary to devise tertiary treatments for their removal. The elimination of impurities by corona oxidation (Innova Process),² UV-light and ozone,³ and batch carbon adsorption¹ are some of the processes already studied and are under pilot plant investigation for large scale application.

Also under investigation is the removal of pollutant compounds by selective adsorption using specific polymers or gels. It is known that adsorptive polymers can be made selective for soluble impurities by preparing them in the presence of the same impurities. Such polymers (silica gels) have been reported for dyestuffs, hormones, and pesticides.⁴⁻⁶ Also, selectively adsorbent cross-linked acrylic polymers have been prepared for dyestuffs⁷ and substituted polystyrenes for optically active sugars.^{8,9}

In this Laboratory silica gels and polyacrylates have been prepared with increased sorption and selectivity for pesticides such as α -chlordane and malathion and for other pollutants, such as p-chlorophenylmethyl sulfone.⁶ The present effort, to prepare specific adsorptive polymers for TNT and the nitramines HMX, and RDX by the above technique, is based on the previous studies.

OBJECTIVE

This investigation pertains to the synthesis of novel polymers and gels in the presence and absence of some priority munitions compounds, and to the testing of these gels and polymers as adsorbents for the removal of the same compounds from aqueous media, such as effluent wastewater.

EXPERIMENTAL

PREPARATION OF NORMAL AND SELECTIVE SILICA GELS

Technical sodium silicate solution (42.0 g), containing 1.4 moles of Na_2O and 4.9 moles of SiO_2 per kg, 42° Be', was weighed out in a 1-liter Erlenmyer flask, mixed with 200 mL distilled water and vigorously stirred while 130 mL of 5.7 N hydrochloric acid was added. After 5 days the stiff gel formed from this solution was broken, washed with methanol, and dried under a slow current of air. The hard, dry, granular material produced in this way was powdered

TABLE 1. CHEMICAL NAMES OF MATERIALS REFERRED TO

Trivial Name	Chemical Name (Chem. Abs.)	Chemical Structure
A. Explosives:		
TNT	2,4,6-trinitrotoluene	
RDX	1,3,5-trinitro-1,3,5-triazine or	
	1,3,5-trinitro-1,3,5-triazacyclohexane	
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocine or	
	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane	
TAX	1-acetylhexahydro-3,5-dinitro-1,3,5-triazine	
SEX	1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine	
B. Monomers:		
	ethyl methacrylate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 = \text{C} - \text{C} - \text{O} - \text{C}_2\text{H}_5 \\ \\ \text{CH}_3 \end{array}$
	ethylene glycol diacrylate	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ \text{CH}_2 = \text{CH} - \text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C} - \text{CH} = \text{CH}_2 \end{array}$
	N,N'-methylene-bisacrylamide	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ \text{CH}_2 = \text{CH} - \text{C} - \text{NH} - \text{CH}_2 - \text{NH} - \text{C} - \text{CH} = \text{CH}_2 \end{array}$
	2,2'-azo-bisisobutyronitrile	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{NC} - \text{C} - \text{N} = \text{N} - \text{C} - \text{CN} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
DMF	N,N-dimethylformamide	$\begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3)_2\text{N} - \text{C} - \text{H} \end{array}$

and sieved. The major portion, between sieve sizes 48 and 200, was first washed by decantation several times with distilled water and then packed in a 10-mm bore glass column and continuously eluted with anhydrous methanol (500 mL). The gel so prepared was allowed to air dry overnight. The yield was 10 to 12 g (12.4 g, theory).

The preparation of the selective silica gels was begun by dissolving in 50 mL of methanol approximately 100 μ mole of the explosive per gram of silica gel expected to result. The quantity of pollutant was 227 mg of TNT, or 222 mg of RDX or 296 mg of HMX. (The presence of methanol does not make any significant structural changes in the gel such as to affect the adsorptive power, as shown by unpublished results.) This solution was added slowly to 42.0 g of sodium silicate solution, with stirring, followed by the addition of 130 mL of 5.7 N hydrochloric acid. The solution of silicate became somewhat cloudy after acidification, showing that the modifiers were incompletely soluble in the polymerizing medium. However, after 5 days the silica gel formed in each case as in the case of the normal gel. The dry selective silica gels were treated in the same way as the normal gel, except that the elution with methanol was followed by elution with acetonitrile (250 mL). This was carried out until the final elution solvent was free of TNT, RDX, or HMX as determined by HPLC. The yield was 10 to 12 g in each case, and this was set aside for testing.

High hydrophilicity is characteristic of silica gels, owing to the presence of OH groups. To increase the affinity of the gels for TNT and nitramines, they were treated with trimethylchlorosilane in the presence of pyridine to block off the OH groups and render them more hydrophobic. For this treatment, approximately 5 g of each of the adsorbents were mixed with a solution of 3 mL of trimethylchlorosilane, 3 mL of pyridine, and 10 mL of n-pentane, and agitated for 3 hours. The mixture was then filtered, washed with n-pentane, methanol, and pentane, and dried in a vacuum oven for 6 hours at 60°C. The prepared samples were labeled as reverse-phase silica gel.

PREPARATION OF NORMAL AND SELECTIVE POLYACRYLATES (CROSS-LINKED)

The monomers for these preparations were ethyl methacrylate, ethylene glycol diacrylate, and N,N'-methylene-bis-acrylamide. The initiator chosen was azobisisobutyronitrile, based on preliminary experimental trials. Choice of monomer and initiator was made on the basis of the ease of polymerization, level of initial presence of inhibitors, and swelling property of the polymers in water. The typical recipe of the monomer mixture was as follows:

CONSTITUENT	MW	PARTS (MOLES)	WT. PARTS
Monomers			
Ethyl methacrylate	114.12	8	5.92 g
Ethylene glycol diacrylate	170.0	3	3.31 g
N,N'-Methylene-bis-acrylamide	154.17	1	1.00 g
Initiator			
2,2'-Azobisisobutyronitrile	164.25	---	0.21 g
Solvent			
DMF (N,N-Dimethylformamide)	73.09	---	35.70 mL

The monomers and initiator were dissolved in the given proportion in DMF in the cold, in a 100 mL screw-capped glass tube, and placed in a constant-temperature bath at 60°C with shaking at half hour intervals. The mixture became milky white and semisolid in 2 hours and solid in 4 hours, after which the tube was heated for 16 hours to complete the polymerization. The solid polymer was removed, powdered, placed in a 10-mm bore glass column, and eluted, first with DMF, then with methanol, and finally with acetone, until all the monomer traces and initiator were removed. Finally, the polymer powder was washed with water and DMF, dried in air, and preserved in a vacuum desiccator for testing.

In the preparation of the selective polymers, 100 µM of pollutant per gram of the monomer mixture was dissolved in the monomer mixture and initiator solution. Polymerization was carried out at 60°C as with the control polymer. In the case of pollutants RDX and HMX, solid polymers formed in 5 to 6 hours; but in the case of TNT this took almost 16 hours. The polymer in each case was powdered, washed as before until free of the modifiers, residual monomers and initiator, dried in air, and preserved in a vacuum desiccator for testing.

TESTING OF THE MODIFIED SILICA GELS AND POLYACRYLATES FOR SPECIFICITY FOR TNT, RDX, AND HMX

The selective and normal (control) polymers were tested for adsorptivity in the following way. A sample of polymer was accurately weighed (0.250 to 0.500 g) in a 50 mL glass-stoppered, tared Erlenmyer flask, and 10 mL of adsorbate solution was added. Adsorbate concentrations ranged from 1.7 to 25 mg/L. The flask was again accurately weighed, stoppered, and placed on a wrist-action shaker for 24 hours. Then the supernatant solution was centrifuged (1,000 rpm) for a half hour to remove the adsorbent, and the concentration of the adsorbate was measured by HPLC. The general procedure followed for HPLC measurement is given below. Pure adsorbate solutions were used in all the adsorption determinations.

The determinations of the substrate concentrations in the adsorption study were made with a high-pressure liquid chromatograph (HPLC), equipped with a UV detector (254 nm 0.01-0.03 AUFS) and fitted with C-18 reverse-phase columns (e.g., µ-Bondapak, Novapak, or Zorbax C-8). The mobile phase was aqueous methanol (20-60% MeOH). The elution rate was 2.0 to 6.0 mL per minute depending upon the retention time. The instrument was calibrated with pure TNT, RDX, and HMX. Correlation coefficients were nearly equal to 1.0, thus ensuring accuracy of the measurements. The same HPLC method was used to evaluate the removal of the adsorbates from adsorbents during the washing and elution process of purifying polymers.¹⁰

The determinations of adsorption of polymer and gel sample were all done in duplicate with very small variation in the adsorption values. An average value has been reported in Tables 2, 3, and 5. However, in Table 4 both the duplicate values have been given as an example of the extent of variation.

Calculation of the adsorptive power of gels and polymers: Adsorptive power is defined⁴ as the ratio of the milligrams of adsorbate per kilogram

TABLE 2. SPECIFIC ADSORPTION BY MODIFIED SILICA GELS
FOR TNT, RDX, AND HMX

Adsorbent	Adsorbate Concentration, mg/L Initial	Equilibrium	Adsorption, mg/kg	Adsorption Power (AP)	$\frac{\text{AP, Modified}}{\text{AP, Control}}$
<u>TNT Adsorption</u>					
Control Gel	25.413	18.640	272.76	14.63	
	12.561	8.699	149.44	17.18	
	6.316	4.209	80.43	19.12	
TNT Modified Gel	25.413	17.440	322.65	18.50	1.26
	12.561	8.178	183.50	22.44	1.31
	6.316	3.647	96.89	22.57	1.18
<u>RDX Adsorption</u>					
Control Gel	19.97	18.62	45.91	2.47	
	10.00	9.08	30.43	3.35	
	4.92	4.62	12.06	2.61	
RDX Modified Gel	19.97	18.51	56.11	3.03	1.23
	10.00	9.06	34.01	3.75	1.12
	4.92	4.49	16.50	3.67	1.41
<u>HMX Adsorption</u>					
Control Gel	7.067	5.99	43.71		
	3.501	3.42	3.31		
	1.764	1.75	0.20		
HMX Modified Gel*	7.067	6.89	7.15		
	3.501	3.48	0.68		
	1.764	1.78	--		

Note: The adsorption power of the solid gel polymer is equal to adsorption (mg/kg) divided by the equilibrium concentration of substrate. Each value reading tabulated is a mean of the two values obtained separately.
* Due to extremely limited solubility of HMX in aqueous media, the results obtained were not consistent.

TABLE 3. SPECIFIC ADSORPTION BY MODIFIED, REVERSE-PHASE SILICA GELS*

Adsorbent	Adsorbate Initial Concentration, mg/L	Equilibrium	Adsorption, mg/kg	Adsorption	
				Power (AP)	AP, Modified AP, Control
<u>TNT Adsorption</u>					
Control Gel	21.54	9.19	136.79	14.88	
	16.15	5.65	205.47	36.37	
	10.69	4.20	126.36	30.09	
	8.03	3.72	83.76	22.52	
TNT Modified Gel	21.54	7.76	267.49	34.47	2.32
	16.15	5.01	209.56	41.83	1.15
	10.69	3.78	129.33	34.21	1.14
	8.03	2.30	107.25	46.63	2.07
<u>RDX Adsorption</u>					
Control Gel	20.83	14.45	117.4	8.13	
	15.49	11.63	72.4	6.23	
	10.49	8.03	42.5	5.29	
	7.51	5.91	31.1	5.26	
RDX Modified Gel	20.83	13.74	128.4	9.35	1.15
	15.49	10.60	93.6	8.83	1.42
	10.29	6.87	60.7	8.84	1.67
	7.51	4.89	46.5	9.51	1.81
<u>HMX Adsorption</u>					
Control Gel	6.500	5.928	10.912	1.841	
	4.881	4.170	14.092	3.379	
	3.194	2.753	8.578	3.116	
	2.413	2.198	4.093	1.862	
HMX Modified Gel**	6.500	6.093	7.462	1.225	0.67
	4.881	4.291	10.860	2.531	0.75
	3.194	3.077	2.110	0.686	0.22
	2.413	2.331	1.506	0.646	0.35

Note: The adsorption power of the solid gel polymer is equal to adsorption (mg/kg) divided by the equilibrium concentration of substrate.

* The values of adsorption are means of two values obtained separately.

** Due to extremely limited and variable solubility of HMX in aqueous media, the results obtained were not consistent and therefore not reliable.

TABLE 4. SPECIFIC ADSORPTION BY MODIFIED POLYACRYLATE POLYMERS (BATCH I)
FOR TNT, RDX, AND HMX

Adsorbent	Adsorbate Concentration, mg/L		Adsorption, mg/kg	Adsorption	
	Initial	Equilibrium		Power (AP)	AP, Modified AP, Control
<u>TNT Adsorption</u>					
Control Polymer	21.41	0.556	792.93	142.61	
TNT Modified Polymers	A 21.41*	9.463	490.52	51.84	0.036
	A 21.41	9.293	496.10	53.38	0.037
	B 5.324	1.747	150.02	85.90	0.060
	B 5.324	1.639	145.66	88.87	0.062
<u>RDX Adsorption</u>					
Control Polymer	20.01	2.096	662.62	316.14	
RDX Modified Polymers	A 20.01	3.974	636.26	160.10	0.51
	A 20.01	3.941	566.51	143.75	0.45
	B 4.967	0.777	147.64	190.01	0.60
	B 4.967	0.747	169.31	226.65	0.70
<u>HMX Adsorption</u>					
Control Polymer	5.189	0.409	199.18	486.99	
HMX Modified Polymers	A 5.189	0.344	173.73	505.02	1.04
	A 5.189	0.375	188.39	502.37	1.03

* The modified polymers are evaluated for adsorption in duplicate.

TABLE 5. SPECIFIC ADSORPTION BY MODIFIED POLYACRYLATE POLYMERS* (BATCH II)
FOR TNT, RDX, AND HMX

Adsorbent	Adsorbate Concentration, mg/L		Adsorption, mg/kg	Adsorption Power (AP)	AP, Modified AP, Control	
	Initial	Equilibrium				
<u>TNT Adsorption</u>						
Control Polymer	21.41	0.05	832.22	1664.4		
	10.71	0.26	459.80	1768.5		
	5.37	0.12	226.49	1887.4		
TNT Modified	21.41	3.06	728.13	238.0	0.14	
	10.71	1.14	339.05	297.4	0.17	
	5.37	0.55	175.59	319.3	0.17	
<u>RDX Adsorption</u>						
Control Polymer	19.156	2.201	733.49	333.3		
	9.460	0.966	367.10	380.0		
	4.758	0.500	187.92	375.8		
RDX Modified	19.156	3.082	691.881	224.5	0.67	
	9.460	1.539	341.292	221.8	0.58	
	4.758	0.718	167.323	233.0	0.62	
<u>HMX Adsorption</u>						
Control Polymer	6.616	0.591	260.65	441.03		
	3.287	0.240	141.27	588.6		
	1.657	0.108	65.45	606.02		
HMX Modified**	6.616	0.195	265.40	1361.03	3.09	
	3.287	0.085	132.48	1558.59	2.65	
	1.657	0.030	70.00	2333.33	3.85	

Note: The adsorption power of the solid gel polymer is equal to adsorption (mg/kg) divided by the equilibrium concentration of substrate.

* The values of adsorption are means of two values obtained separately.

** The values of HMX adsorption are not reliable due to very low and variable solubility of HMX in water.

(mg/kg) of the adsorbent to the milligrams per liter (mg/L) of adsorbate in the solution in equilibrium with the saturated adsorbent. It is calculated as follows:

$$AP = \frac{(I_C - F_C)}{W_A \times F_C} W_S$$

where AP = Adsorptive power

I_C = Initial substrate concentration in ppm (mg/liter)

F_C = Final substrate concentration in (mg/liter)

W_S = Weight in grams of substrate solution

W_A = Weight of the adsorbent in grams

In this study mg/L, ppm, and mg/kg are taken to be equivalent to each other considering the low concentration of the substrate in water (only in case of water solution for comparison to adsorption by solids).

The relative adsorptive power is given by the ratio of the adsorptive power of the selective polymer or gel to the adsorptive power of the normal (unmodified) polymer or gel. These quantities are included in the Tables wherever applicable.

RESULTS AND DISCUSSION

The adsorptivity of a polymer for a chemical compound is found to be significantly increased when the polymer is prepared in a system containing the compound in homogeneous solution. Silica gel is made with increased sorption for dyestuffs such as methyl orange or ethyl orange and cross-linked polyacrylates, for safranin and rhodanite blue. In the work reported here, it was proposed to make selective silica gels and cross-linked polyacrylates and to study these as possible adsorbents for TNT, RDX, and HMX. For munitions compounds this is a new approach; thus it may not have the potential of immediate translation into a large scale industrial process, but it stands a chance of being a widely applicable process of making adsorbents for a variety of such pollutants. The dependence of the adsorptivity on molecular proportion of the impurities in preparation, solubility, interaction, and molecular motion (depending upon temperature), are factors to be studied later.

Adsorption determinations made with silica gels gave consistently higher adsorption of TNT and RDX to the modified adsorbents than to the normal ones (Table 2). This was increased further by the trimethylchlorosilane treatment of the gels, which blocks OH groups and thus increases affinity for TNT and nitramines (Table 3).

Aqueous solutions of highly acidic sodium silicate slowly polymerize to form the silica gel structure, with large numbers of oxide and hydroxide groups, whose structure decides the form of the template for the adsorbate molecules in solution. Formation of templates can be conceivably dependent upon the number of adsorbate molecules in solution (TNT or nitramines) and the fact that growth of polymer structure is somewhat faster than the thermal agitation of the adsorbate solution. The amount of the template forming

adsorbates available to the polymer formed should be at least 100 μM per gram to give the polymer a maximum specific adsorptivity of about 20% of its weight (200 g per kg).⁷ The nitramines or TNT are not soluble in water to even 10^{-4} times this; therefore, one can understand the low increase in the specific adsorptivity of the SiO_2 gels made, as reported in Table 2.

In the case of the preparation of specific silica gel adsorbents for TNT, RDX, and HMX, the method of increasing the adsorptivity of modified gels seems to be to increase the solubility of the pollutants in the aqueous media in which silica gel is formed, by incorporation of alcohols, acetone, DMF, or even DMSO, in the media.

In the experiments with modified cross-linked polyacrylates (Table 4), it was observed that the adsorptivity of the modified polymers with TNT and RDX decreased rather than increased, as expected, from their normal adsorptivity. This opposite effect may be interpreted as being due to the inhibition of polymerization or to high chain transfer coefficients attributed to TNT and RDX.¹¹ However, HMX modification of the polymers showed the expected significant increase in adsorptive power. This result indicates that the free-radical type polymerization may not be successful in case of TNT and RDX, due to chain-transfer interference,¹¹ and therefore a cationic or anionic polymerization should be considered to obtain highly adsorbent polymers for these pollutants. This does not seem to apply to HMX, for which it was possible to produce specific adsorbent, cross-linked polyacrylate.

The decrease in adsorption power of the polyacrylates was observed in the first batch of polymers prepared as reported in Table 4. Then the polymers were prepared again (batch 2), evaluated, and reported in Table 5. The results were the same excepting the results for HMX, which were not reproducible.

RECOMMENDATIONS

1. Preparation of the modified cross-linked polyacrylates should be attempted in the presence of TNT and RDX by the cationic or anionic process of polymerization, where the inhibitory action of TNT and RDX may be avoided, to obtain highly adsorptive polymers.
2. The aqueous media of silica gel formations should be mixed with alcohols, acetone, dimethyl formamide, or dimethylsulfoxide to increase the solubility of the pollutants (TNT, RDX, and HMX).
3. Further study should address the effect of increasing the molecular proportion of TNT, RDX, and HMX in the polymerizing media on the resulting adsorptivity of the polymer.

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